

Seasonal, Daily and Intradiurnal Variation of PM₁₀, NO₂, NO and O₃ in Residential Part of Zagreb, Croatia

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ABSTRACT

Pollutants such as particulate matter, nitrogen oxides, carbon oxides, ground-level ozone, etc. are harmful to human health. Study of pollutant variation and its relationship with both dynamic and thermodynamic atmospheric boundary layer (ABL) structures is of importance not only for environmental protection but also for the public at large. The aim of this study was to analyze seasonal, daily and intradiurnal variation of PM₁₀, NO₂, NO and O₃ in a residential part of an urban area, and the effect of some meteorological parameters. The study was conducted from January 1 till December 31, 2004 in the City of Zagreb using following methods: beta radiation absorption, chemiluminescence and UV photometry. The results presented in this article, show the dependence of air pollution levels upon traffic density, seasons and meteorological conditions. Considering the level of air pollution relative to the regulated limit and tolerated values, the measured 24-hour concentrations of all study pollutants exceeded the borderline values and/or tolerated values, however, the number of days with such pollutant concentrations did not exceed the allowed frequency. This is a preliminary study with the main objectives to point to the possible identification of the source of pollution and to assess the level of air contamination according to the new national legislation coordinated with European regulations. Future measurements and studies should evaluate in detail the causes of the concentration levels detected.

Key words: air pollution, particulate matter (PM₁₀), nitrogen oxides, ozone, health risk, meteorological parameters

Introduction

Air pollution is always a public concern, especially in urban areas. Air pollution is mainly caused by the sources of pollutant emission and by weather conditions such as the atmospheric boundary layer (ABL) stability, wind speed and direction, turbulence, temperature, precipitation, humidity, topography, etc¹. Study of pollutant variation and its relationship with both dynamic and thermodynamic ABL structures is of importance not only for environmental protection but also for the public at large. It is well known that pollutants such as particulate matter, nitrogen oxides, carbon oxides, ground-level ozone, etc. are harmful to human health in different ways.

Airborne particulate matter (PM), a mixture of organic and inorganic substances, originates from a variety of sources such as power plants, industrial processes and

diesel trucks, and is formed in the atmosphere by transformation of gaseous emissions. PM concentration measured as PM₁₀ (which includes fine and coarse particles) originates not only directly from combustion processes but also from resuspension from street surfaces. In spring, after the snow has melted and streets dry out, particles from street surfaces are resuspended by traffic induced turbulence and wind^{2,3}. In northern and Central European cities, resuspended particulate matter can have a substantial influence particularly on total suspended particles but also on PM₁₀ concentrations^{4,5}. Their chemical and physical composition depends on the location, time of year, and weather. Historically, the association between PM₁₀ and mortality has been manifested in many air pollution episodes. Several studies demonstrated the

relationship between low concentrations of PM₁₀ and increase in daily mortality and morbidity^{6–8}, and between PM₁₀ exposure and increase in bronchitis, chronic cough, and respiratory symptoms in persons with chronic obstructive pulmonary disease^{9,10}. The term »nitrogen oxides« refers to a group of oxides formed in the combustion process, the principal constituents of which are nitrogen monoxide (NO) and nitrogen dioxide (NO₂). The majority of nitrogen oxides emitted from vehicle exhausts are in the form of NO. This gas can react with unburned hydrocarbonates, also present in the exhaust, to form NO₂. NO is not considered harmful at ambient concentrations. NO₂ is a reactive pollutant formed by oxidation of atmospheric nitrogen during fuel combustion at high temperature and a key component for the rise of secondary toxic pollutant (nitric acid, the nitrate part of secondary inorganic aerosols and photo-oxidants including ozone). It is also known that concentrations of NO₂ in ambient air and its potential mixtures can enhance the effects of other environmental pollutants and allergens. The health risks posed by nitrogen oxides may potentially result from NO₂ itself or its reaction products including O₃ and secondary PM. Additionally, NO₂ concentrations closely follow vehicle emissions in many situations so that NO₂ levels are generally a reasonable marker of exposure to traffic related emissions. Epidemiologic studies have provided some evidence that long-term NO₂ exposure may impair pulmonary function and increase the risk of respiratory symptoms. In most of these studies, NO₂ concentrations at the community level were correlated with PM and ozone^{11–15}. Ozone is the most important photochemical oxidant in the troposphere. It is formed by photochemical reactions in the presence of precursor pollutants such as NO_x and volatile organic compounds. Ozone has harmful effects on vegetation and human health. There is evidence for a significant association between short-term peaks in ambient air concentra-

tions of O₃ and lung epithelial damage¹⁶. Long-term effects of ozone on human health include an increased incidence of asthma and lung cancer, impaired pulmonary function, etc.¹⁷.

In the present study, seasonal, daily and intradiurnal variation of PM₁₀, NO₂, NO and O₃ was analyzed in a residential part of an urban area. The effect of some meteorological parameters (temperature and precipitation) on these concentrations was also investigated.

Material and Methods

Measuring site and period

The study was conducted from January 1 till December 31, 2004 in the City of Zagreb with 779,145 inhabitants (as *per* 2001). Zagreb is situated on the southern hills of the Medvednica mountain (1000 m above the sea level), extending towards the Sava valley on the south. Air sampler was placed in the northern, residential part of the City of Zagreb (Gauss-Krüger coordinates: 050-76-794 N; 055-76-542 E; 175 m above the sea level), at >5 m distance from a street with moderate traffic intensity and 400 m distance from a crossing with high traffic intensity.

Sampling and measuring methods

Particulate matter PM₁₀ was measured by the method of beta radiation absorption (Automated Equivalent Method: EQPM-0404-151) on an Environment S.A. Model MP101M PM₁₀ Beta Gauge Monitor device¹⁸. NO₂ and NO were measured by the method of chemiluminescence (Automated Reference Method: RFNA-0795-104) on an Environment S.A. Model AC31M chemiluminescence nitrogen oxide analyzer¹⁹. O₃ was measured by the method of UV photometry (Automated Equivalent Method: EQOA-

TABLE 1
MONTHLY VARIATION OF 24-HOUR POLLUTANT CONCENTRATIONS IN ZAGREB-MIROGOJSKA, 2004

	Pollutant/24-hour concentrations (mgm ⁻³)											
	Particulate matter (PM ₁₀)			Nitrogen dioxide (NO ₂)			Nitrogen monoxide (NO)			Ozone (O ₃)		
	Min.	Max.	\bar{X}	Min.	Max.	\bar{X}	Min.	Max.	\bar{X}	Min.	Max.	\bar{X}
Jan	12.81	59.94	31.54	4.96	73.09	34.93	4.19	57.76	26.23	4.44	49.36	25.11
Feb	16.47	76.63	28.50	8.26	70.42	38.77	2.99	114.26	22.88	5.67	70.42	38.77
Mar	11.66	45.23	28.88	10.26	56.85	29.22	2.92	34.74	12.13	31.74	93.59	57.27
Apr	12.70	49.96	23.52	5.09	35.84	23.74	2.92	22.04	11.11	42.52	83.82	61.88
May	12.83	40.49	19.49	6.83	44.02	19.24	2.20	16.63	8.42	48.61	104.64	73.89
Jun	12.52	28.5	18.56	8.00	28.68	15.50	2.40	12.12	5.88	47.17	113.96	71.33
Jul	11.51	34.01	21.42	3.87	25.14	15.23	1.76	15.08	5.93	45.47	112.28	75.34
Aug	11.94	33.21	21.06	5.23	27.05	13.66	2.11	11.03	5.34	49.56	91.39	70.27
Sep	16.19	45.85	30.48	5.55	33.22	18.14	2.20	38.86	11.36	24.41	93.12	50.37
Oct	15.16	62.89	35.33	6.99	35.75	23.79	4.70	57.90	23.90	6.11	39.97	22.51
Nov	13.30	108.66	41.31	2.16	50.32	26.39	2.73	128.10	29.28	2.27	56.93	23.94
Dec	16.93	84.18	42.59	13.57	45.32	28.29	7.32	65.53	31.86	3.74	44.16	17.02

-0206-148) on an Environment S.A. Model O₃42M UV ozone analyzer²⁰. The values of air temperature were also recorded. Data on daily precipitation were provided by the Croatian Weather Bureau – Grič Observatory, located about 1 km from the measuring site. The ambient air quality was compared with the National Air Quality Standards²¹ to be enacted in 2006.

Results

During 2004, the measured concentrations of airborne pollutants showed quite a regular pattern. During the winter, the highest 24-hour air concentrations were recorded for the following pollutants: PM₁₀ (31.54–42.59 µgm⁻³), NO₂ (28.29–38.77 µgm⁻³) and NO (22.88–31.86 µgm⁻³). In summer, these pollutants showed lowest 24-

hour concentrations: PM₁₀ 18.56 µgm⁻³, NO₂ 13.66 µgm⁻³, and NO 5.34 µgm⁻³. An inverse pattern was only observed for ozone (O₃), as lowest concentrations of this pollutant were recorded in winter (17.02–23.94 µgm⁻³) and highest in summer (71.33–75.34 µgm⁻³) (Table 1).

The effect of meteorological parameters, especially precipitation, on airborne pollutant concentrations was observable throughout the year. The concentration of pollutants decreased abruptly on days with precipitation (Figure 1).

According to the National Air Quality Standards, the concentration of PM₁₀ exceeded the limit value (LV) of >50 µgm⁻³ on 17 occasions, and the margin of tolerance (tolerated value, TV) on 3 occasions during the calendar year. The concentrations of other pollutants (NO₂ and O₃) also were within the allowed limits of excess (Table 2).

TABLE 2
POLLUTANT EXCEEDENCE IN ZAGREB-MIROGOJSKA, 2004

	Pollutant					
	Particulate matter (PM ₁₀)		Nitrogen dioxide (NO ₂)		Ozone (O ₃)	
Values (24-hour average)	TV >75 µgm ⁻³	GV >50 µgm ⁻³	TV >120 µgm ⁻³	GV >80 µgm ⁻³	TV >110 µgm ⁻³	GV N/A
Number of days	3	17	0	1	3	
Range of conc. (mgm ⁻³)	75.63–108.66	50.48–108.66	0	83,46	110.27–121.97	
Month	Feb, Nov, Dec	Jan, Feb, Oct, Nov, Dec	0	Feb	Jun, Jul	
Regulatory limit	Not to be exceeded more than 35 times a calendar year		Not to be exceeded more than 7 times a calendar year		Not to be exceeded more than 7 times a calendar year	

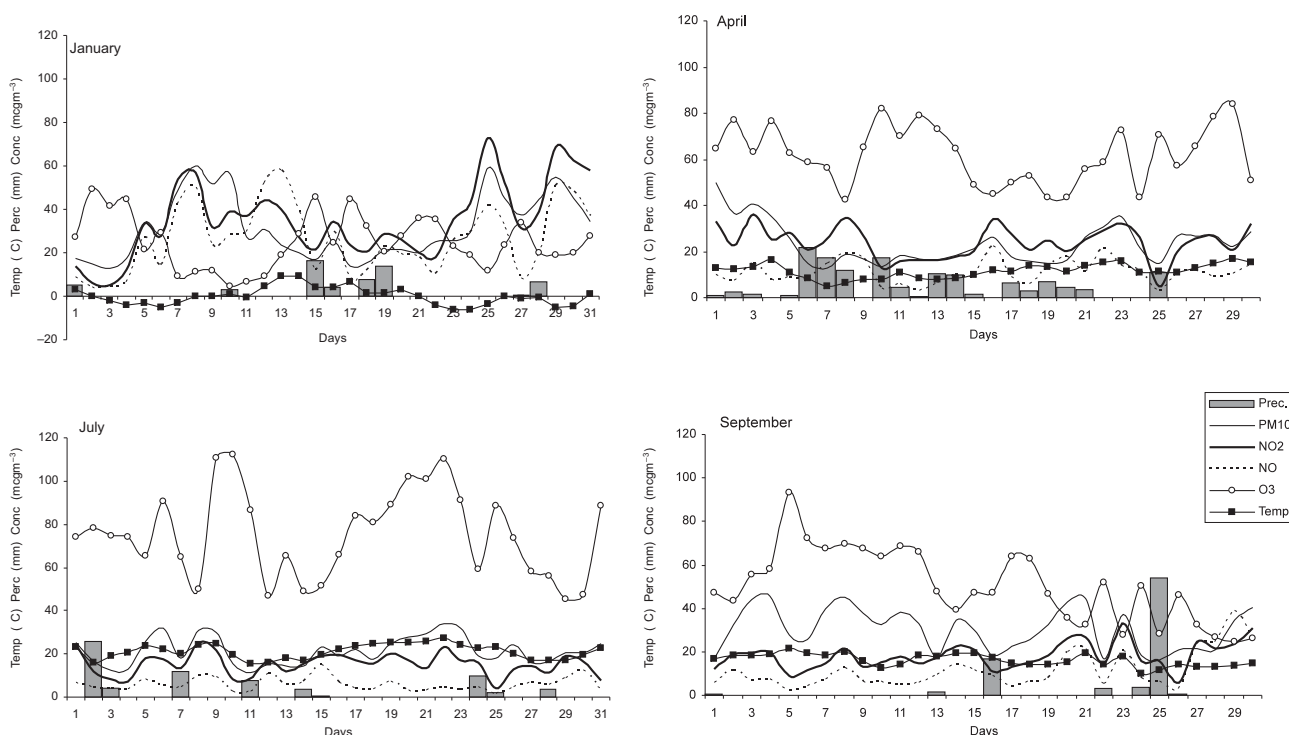


Fig. 1. Daily variation of 24-hour pollutant concentrations, mean temperature and precipitation during 2004 (Zagreb, Mirogojska 16).

The mean 24-hour PM₁₀, NO₂ and NO concentrations showed a rising tendency towards mid-week, with a peak on Wednesday (31.12 $\mu\text{g m}^{-3}$; 28.29 $\mu\text{g m}^{-3}$; and 19.84 $\mu\text{g m}^{-3}$) and minimal value on Sunday (24.11 $\mu\text{g m}^{-3}$; 17.89 $\mu\text{g m}^{-3}$; and 9.86 $\mu\text{g m}^{-3}$), whereas an inverse pattern was observed for O₃ (peak on Sunday, 72.23 $\mu\text{g m}^{-3}$, and minimal value on Wednesday, 45.62 $\mu\text{g m}^{-3}$). The same pattern was recorded in winter and summer, only the concentrations of PM₁₀, NO₂ and NO were lower and those of O₃ higher in summer (Figure 2). Intradiurnal curves of average hour concentrations of PM₁₀, NO₂ and NO were quite comparable, with two peaks (in the morning and in the afternoon) and lower values in summer. The only exception was the O₃ curve, showing one peak in the afternoon and higher values in summer. In winter, PM₁₀ reached first peak concentration (43.3 $\mu\text{g m}^{-3}$) at 11.00 a.m. (in summer at 12.00 a.m.), and second peak concentration (46.7 $\mu\text{g m}^{-3}$) at 7.00 a.m. (in summer at 9.00 a.m.), whereas the lowest PM₁₀ concentration was recorded at 5.00 a.m. The values of intradiurnal concentrations were lower in summer (April–September). NO₂ reached the first peak concentration at 10.00 a.m. in winter (36.0 $\mu\text{g m}^{-3}$) and at 9.00 a.m. in summer (39.1 $\mu\text{g m}^{-3}$); and second peak concentration at 6.00 p.m. in winter (39.1 $\mu\text{g m}^{-3}$) and at 9.00 p.m. in summer (25.0 $\mu\text{g m}^{-3}$). An

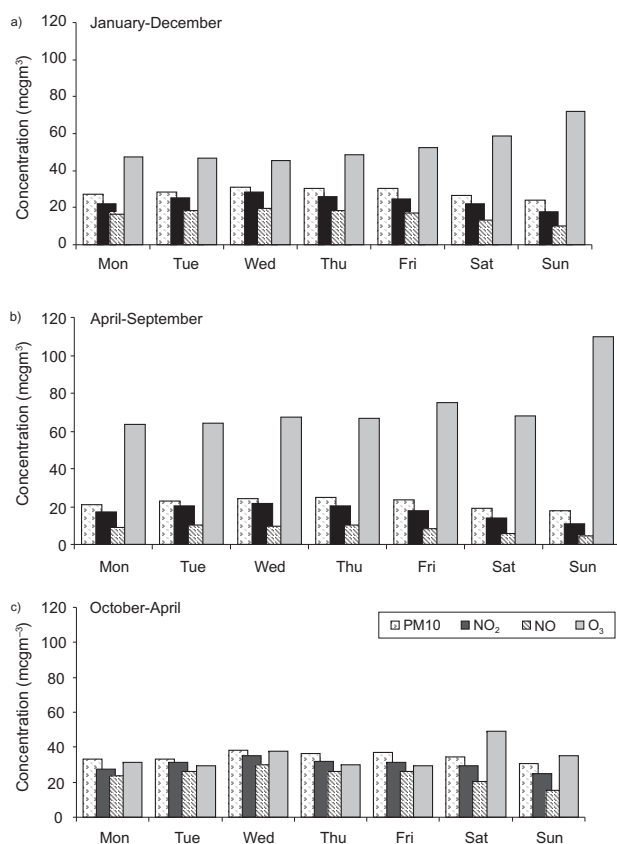


Fig. 2. Weekly variation of 24-hour pollutant concentrations a) annual, b) summer, c) winter.

identical pattern was observed for NO. The lowest concentrations of these pollutants were also recorded at 5.00 a.m. O₃ showed lowest concentrations at 8.00 a.m., to slowly rise until 4.00 p.m. (96.76 $\mu\text{g m}^{-3}$ in summer and 43.83 $\mu\text{g m}^{-3}$ in winter) and declining thereafter. The summer curve was characterized by an abrupt overnight increase to 58.43 $\mu\text{g m}^{-3}$ at 1.00 a.m. and 80.74 $\mu\text{g m}^{-3}$ at 2.00 a.m., followed by a decrease to 59.75 $\mu\text{g m}^{-3}$ at 3.00 a.m. (Figure 3). The curves showed a similar pattern of intradiurnal distribution of the mean pollutant concentrations during work-days (Mon–Fri) and weekend (Sat–Sun) throughout 2004. Air concentrations of PM₁₀, NO₂ and NO were higher on workdays (most pronounced in NO and NO₂ curves), and those of O₃ on weekends (slight difference from work-days) (Figure 4).

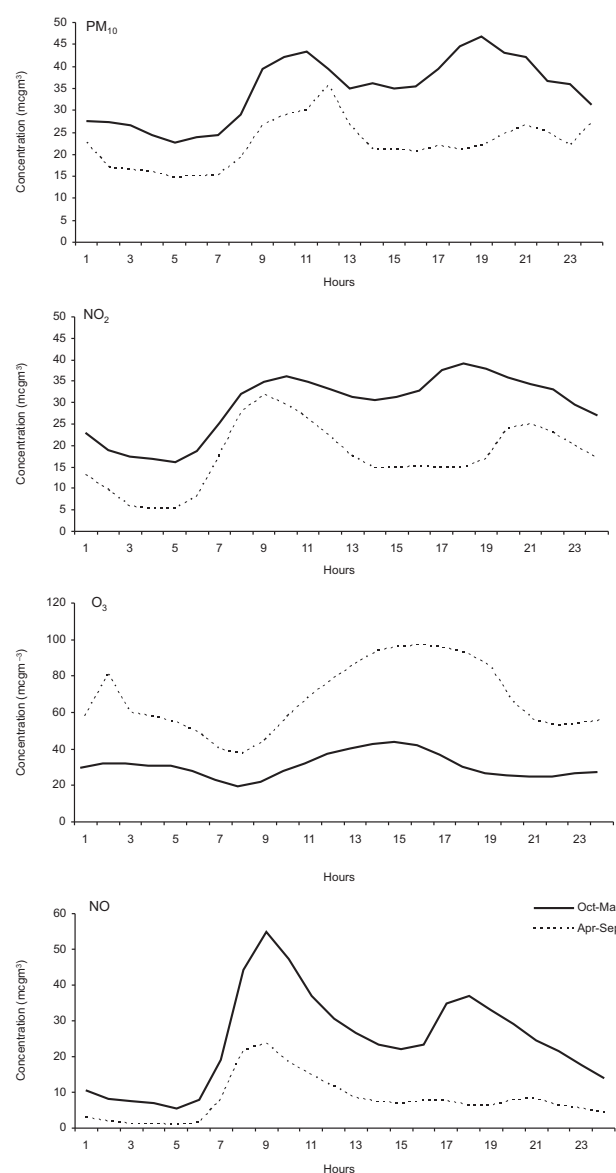


Fig. 3. Intradiurnal hourly concentrations of PM₁₀, NO₂, O₃ and NO during winter and summer (2004).

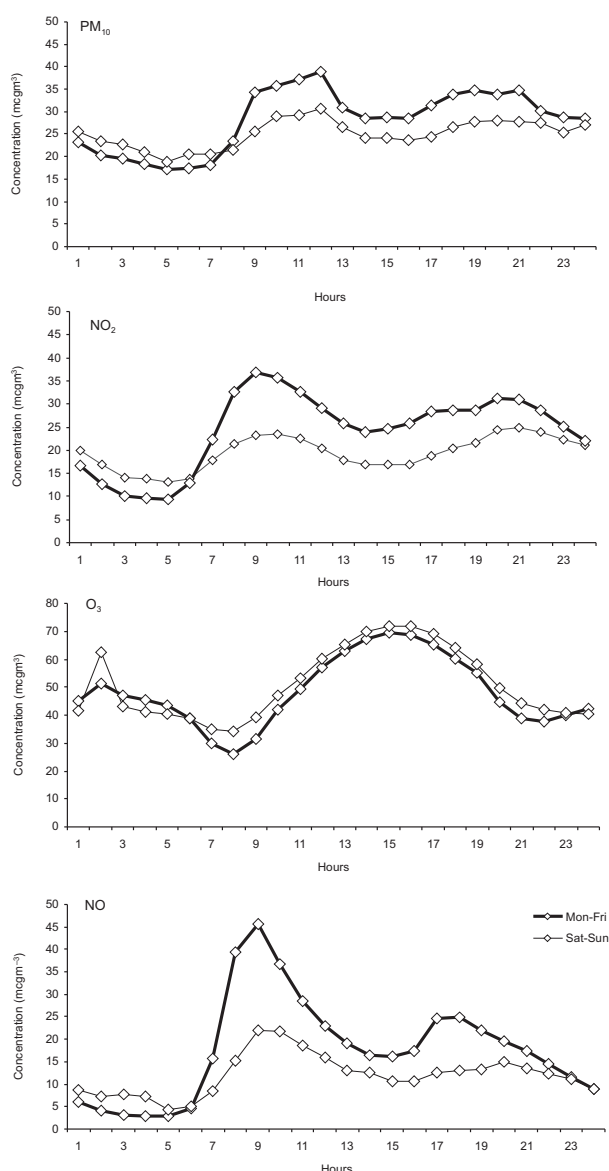


Fig. 4. Intradaily hourly concentrations of PM₁₀, NO₂, O₃ and NO during working and weekend days (2004).

Discussion

The results of seasonal variation in 24-hour concentrations of PM₁₀, NO₂ and NO, indicating higher values in winter, could be explained by air pollution from two emission sources characteristic of the measuring site located in the residential area with moderate traffic intensity and a number of public institutions boiler-rooms of a medium size. A correlation of some meteorological parameters with variation in the concentration of the study pollutants was recorded in all seasons. In winter, the concentration of pollutants increased with temperature decline, especially on precipitation-free days. Similar results have been reported in a study of diurnal and seasonal variation of CO and NO₂ in Delhi²². The rise in

PM₁₀ concentration recorded in September was ascribed to the increased traffic intensity upon return of the majority of the Zagreb residents from their summer holiday and a small number of rainy days. The greater increase of PM₁₀ concentration was probably consequential to the growing number of resuspended particles due to dry weather⁴. The regular diurnal pattern of 24-hour PM₁₀ and NO₂ concentrations observed during the week, and of intradiurnal concentrations was directly related to traffic intensity. It was indicated by elevated concentrations towards mid-week and evident presence of two peak intradiurnal concentrations in the morning and in the afternoon. This phenomenon was especially pronounced in winter, characterized by higher traffic intensity²³ and more harmful operation of internal-combustion engines. Comparison of intradiurnal concentrations between summer and winter will be used in future studies to identify the rate of particular sources of pollution in the area.

Ozone is influenced by seasonal and diurnal variation. In our study, ozone concentration showed clear peaks in spring and summer, with the mean 24-hour concentrations in spring and summer twofold and threefold those measured in Vancouver, respectively, where annual peak was recorded in May (in Zagreb in July)²⁴. The concentrations decreased towards autumn, to be lowest during winter. Also, higher levels of nitrogen oxides were associated with lower ozone concentrations. This situation reflected primary reactions involving ozone and ozone precursors in urban areas. A similar pattern has been reported from northern Europe, however, summer peak was not as clear²⁵. The intradiurnal behavior during spring and summer (April–September) reflected sunshine and daily temperature, whereas during night the wind velocity was the most important driving force for the presence of ozone, i.e. when the mixing effect of the wind is low or diminished, the ozone is deposited into the vegetation due to its strong oxidizing potential²⁶. Considering the level of air pollution relative to the regulated limit and tolerated values, the measured 24-hour concentrations of all study pollutants exceeded the borderline values and/or tolerated values, like those reported from Portuguese urban agglomerations however, the number of days with such pollutant concentrations did not exceed the allowed frequency²⁷. In the present study, a part of the results collected during the first year of measurement at this site were processed, so it was a preliminary study with the main objectives to point to the possible identification of the source of pollution and to assess the level of air contamination according to the new national legislation coordinated with European regulations. Future measurements and studies should evaluate in detail the causes of the concentration levels detected.

Conclusions

1. During the winter, the highest 24-hour air concentrations were recorded for the following pollutants: PM₁₀, NO₂ and NO. An inverse pattern was observed for ozone O₃.

2. The effect of meteorological parameters, especially precipitation, on airborne pollutant concentrations was observable throughout the year. The concentration of pollutants decreased abruptly on days with precipitation.

3. The mean 24-hour PM₁₀, NO₂ and NO concentrations showed a rising tendency towards mid-week, with a peak on Wednesday and minimal value on Sunday, whereas an inverse pattern was observed for O₃.

4. Intradiurnal curves of average hour concentrations of PM₁₀, NO₂ and NO were quite comparable, with two

peaks (in the morning and in the afternoon) and lower values in summer. The only exception was the O₃ curve, showing one peak in the afternoon and higher values in summer.

5. The curves showed a similar pattern of intradiurnal distribution of the mean pollutant concentrations during workdays (Mon-Fri) and weekend (Sat-Sun). Air concentrations of PM₁₀, NO₂ and NO were higher on workdays, and those of O₃ on weekends.

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SEZONSKE, DNEVNE I INTRADIURNALNE VARIJACIJE PM₁₀, NO₂, NO I O₃ U STAMBENOJ ČETVRTI GRADA ZAGREBA, HRVATSKA

SAŽETAK

Onečišćujuće tvari kao što su lebdeće čestice, dušikovi oksidi, ugljikovi oksidi, prizemni ozon i dr. štetni su za ljudsko zdravlje. Svrha ovog rada je analizirati sezonske, dnevne i intradiurnalne varijacije PM₁₀, NO₂, NO i O₃ u stambenoj četvrti urbanog područja, kao i učinak nekih meteoroloških parametara na koncentraciju ovih onečišćujućih tvari. Istraživanje se provodilo u razdoblju od 1. siječnja do 31. studenoga 2004. godine u Gradu Zagrebu, a koristile su se sljedeće metode: apsorpcija beta radijacije, kemiluminiscencija i UV fotometrija. Rezultati prezentirani u ovom radu pokazuju povezanost razina onečišćujućih tvari s gustoćom prometa, sezonama i meteorološkim uvjetima. 24 satne koncentracije svih mjerenih onečišćujućih tvari u zraku prekoračuju granične i/ili tolerantne vrijednosti definirane zakonskom regulativom, ali broj dana s prekoračenjem koncentracija onečišćujućih tvari u granicama je dozvoljenih učestalosti. Ovaj rad predstavlja preliminarna istraživanja s ciljem identifikacije izvora onečišćenja kao i utvrđivanje razina onečišćenja prema novoj nacionalnoj legislativi koja je usklađena s Europskom regulativom.